

CRYSTALLINITY OF POLY(VINYL STEARATE)

It is well known that poly(vinyl stearate) at ordinary temperatures is a waxy, weak, brittle polymeric substance. This indicates a relatively high degree of crystallinity. A search of the literature revealed no information on the x-ray diffraction spectrum nor the amount and size of crystallites found within homopolymers containing long aliphatic side chains. This note is to report the x-ray diffraction spectrum at room temperature and the per cent crystallinity and crystallite size at various temperatures of unoriented poly(vinyl stearate).

The sample of poly(vinyl stearate) used was prepared by emulsion polymerization (1). Specimens suitable for the x-ray investigation were prepared in a sandwich-type mold using cellophane to prevent sticking, heated to about 65°C. for about 1 min., molded under low pressure, and cooled slowly to room temperature. The sample dimensions were about $1 \times 1 \frac{1}{2} \times 0.05$ in. A General Electric XRD-3 direct recording diffractometer was used. Nickel filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$.) 1° beam slit, 0.2° detector slit, medium resolution soller slit, 5 min./degree scanning speed, 12 in./hr. chart speed, linear scale, 4-sec. time constant. The area under the peaks of the diffractometer tracing was measured by counting with a Berkeley automatic scaler, Model 2200-2. (Mention of specific commercial firms or products does not imply endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.) Temperature of the specimen was maintained at $\pm 0.5^\circ\text{C}$. by passing thermostatically heated water through a hollow

TABLE I

X-Ray Diffraction Data of Poly(Vinyl Stearate)

Angle (degrees 2θ)	Interplanar spacing, A.	Relative intensities ^a
5.7	15	70
9.2	9.6	30
21.3	4.2	1000
39.5	2.3	20

^a Relative intensities are measured as counts per second at the maximum height of the peak minus counts per second for the background, and then expressed on a relative scale with the strongest maxima arbitrarily given a value of 1000.

brass block on which the specimen rested. The surface of the sample was at about the same temperature as the bulk.

Given in Table I is the x-ray diffraction data obtained from poly(vinyl stearate). Four diffraction maxima are shown; two are relatively sharp and well defined, namely, those with interplanar spacings at 15 and 4.2 Å. The other two peaks, however, were relatively weak and diffuse. Examination of the relative intensities of interplanar spacings shows that the 4.2 Å. diffraction maximum is very much stronger than the other three. This spacing is essentially the same found for many simple long-chain aliphatic compounds (2).

The per cent crystallinity of unoriented poly(vinyl stearate) was determined by the Aggarwal and Tilley (3) continuous counting method. The 4.2 Å. ($2\theta = 21.2^\circ$) peak was taken as the crystalline peak, and the position of the amorphous peak was taken as 4.6 Å. ($2\theta = 19.4^\circ$). The position of the amorphous peak was arrived at by examination of the x-ray diffraction pattern of unoriented poly(vinyl stearate) taken very near the melting point which is 52° – 54°C . The amorphous maximum of unoriented poly(vinyl stearate) is at about the same position as is the amorphous maximum of polyethylene; however, the position of the maximum of the crystalline region is somewhat different (2). The calculations of the per cent crystallinity are based upon the following measurements and assumptions. Total counts were taken from 5.90 Å. ($2\theta = 15.00^\circ$) to the center of the 4.2 Å. ($2\theta = 21.2^\circ$) peak, and from the center of the 4.2 Å. ($2\theta = 21.2^\circ$) peak to 2.98 Å. ($2\theta = 30.00^\circ$). Background was measured by counting for 100 sec. at $2\theta = 15.01^\circ$ and at $2\theta = 29.99^\circ$. The background was assumed to vary linearly over the entire range and was subtracted out. The remaining counts from 5.90 Å. ($2\theta = 15.00^\circ$) to 4.2 Å. ($2\theta = 21.2^\circ$) were assumed to contain counts due to the amorphous peak and one-half of the crystalline peak. The remaining counts for 4.2 Å. ($2\theta = 21.2^\circ$) to 2.98 Å. ($2\theta = 30.00^\circ$) were assumed to contain the counts due

TABLE II

Per Cent Crystallinity and Crystallite Size of
Poly(Vinyl Stearate)

Temperature, $^\circ\text{C}$.	Crystallinity, %	Crystallite Size, Å.
28	89	75
35	88	83
40	87	83
44	82	83
45	80	87
46	69	87

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to one-half the crystalline peak. Integrated intensities were corrected for lorentz and polarization factors (4) but not for temperature, etc., as these were considered negligible in the present work. The calculated per cent crystallinity at room temperature was about 89. Duplicate determinations made at room temperature using the same sample gave the same value of per cent crystallinity, but when different samples of poly-(vinyl stearate) were used the calculated per cent crystallinity differed by 2%.

The variation in crystallinity with temperature was investigated. As shown in Table II the per cent crystallinity remained essentially constant from room temperature to about 40°C. Between 40 and 45°C. the amount of crystallinity decreased slowly with temperature and attained a value of 80% at 45°C. Above 45°C. the per cent crystallinity decreased sharply. We were unable to accurately measure the per cent crystallinity much above 46°C. because the specimen flowed. This is probably due to the fact that the sample is too near the melting point.

The average crystallite size in unoriented poly(vinyl stearate) was determined from line broadening (4). The 4.2 Å. ($2\theta = 21.2^\circ$) peak was used, the constant of proportionality K in the general equation $D = 57.3 K / \beta_{1/2} \cos \theta$ was assumed to be 0.9 as recommended by Klug and Alexander (5). The calculated average crystallite size at room temperature was surprisingly small, about 75 Å.

From Table II it can be seen that the average crystallite size increases with increasing temperature. This would be expected if a wide distribution of crystallite sizes were produced on cooling from the molding cycle. The smaller crystallites would melt out at the lower temperatures, fuse together, and form larger crystallites as the sample was conditioned at a slightly higher temperature.

References

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